

(19) World Intellectual Property Organization
International Bureau



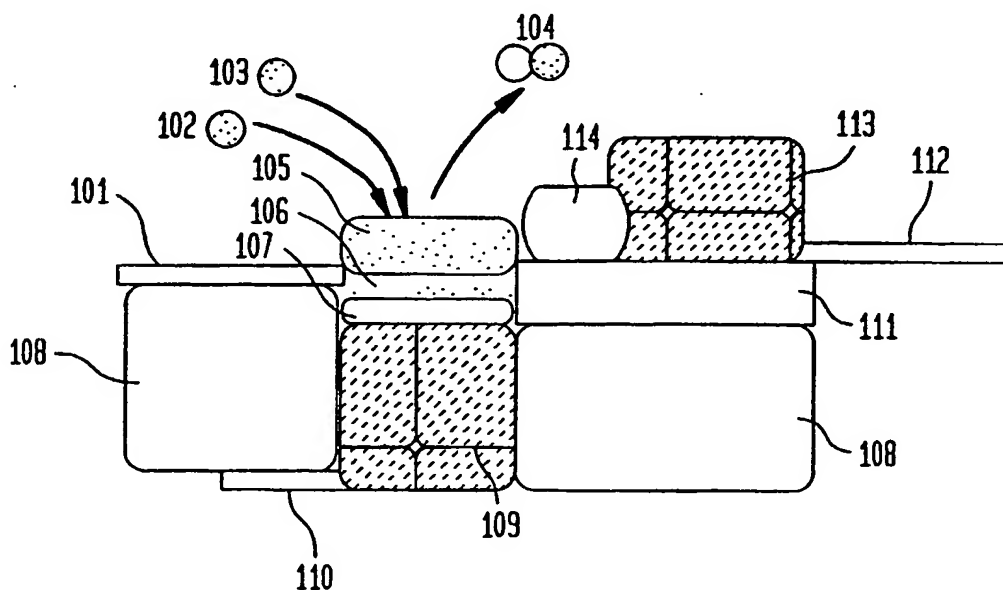
(43) International Publication Date
30 November 2000 (30.11.2000)

PCT

(10) International Publication Number
WO 00/72384 A1

- (51) International Patent Classification⁷: H01L 31/00
- (21) International Application Number: PCT/US00/11119
- (22) International Filing Date: 25 April 2000 (25.04.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/304,979 4 May 1999 (04.05.1999) US
- (71) Applicant: NEOKISMET L.L.C. [US/US]; Suite 1350,
456 Montgomery Street, San Francisco, CA 94104 (US).
- (72) Inventors: ZUPPERO, Anthony, C.; 6854 East Sunnyside Road, Idaho Falls, ID 83406 (US). GIDWANI, Jawahar, M.; 2335 Leavenworth, San Francisco, CA 94133 (US).
- (74) Agents: PARK, Eunhee et al.; Baker & McKenzie, 805 Third Avenue, New York, NY 10022 (US).
- (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PRE-EQUILIBRIUM CHEMICAL REACTION ENERGY CONVERTER



(57) Abstract: The use of newly discovered chemical reaction products (102, 103, 104), created when reactants combine to form products on the surface of a catalyst (105), to generate electricity, beams of radiation, or mechanical motion. The invention also provides methods to convert the products into electricity or motion.

WO 00/72384 A1

BEST AVAILABLE COPY

PRE-EQUILIBRIUM CHEMICAL REACTION ENERGY CONVERTER

5 Field Of The Invention

The present invention relates to the extraction of electrical or mechanical energy or coherent radiation from chemical reactions occurring on the surface of a catalyst before thermal equilibrium has been reached by the forms of
10 the released energy.

Background Information

Recent experimental observations have revealed clues to various catalytic processes occurring: 1) during the 0.01
15 pico-second time interval during which chemical reactants form bonds with the surface of a catalyst, causing the emission of charge carriers, such as electrons and holes; 2) during the picosecond time interval during which reactants adsorb and lose energy in quantum steps after becoming trapped at a
20 potential well between an adsorbate and a catalyst surface, producing electronic friction, charge carrier currents and phonon emission; and 3) during the nanosecond and longer time intervals during which reaction intermediates and products radiate electromagnetic energy, either while trapped on a

catalyst surface or immediately after escaping it. These processes entail three energy releasing processes, namely: 1) charge carrier emission (electrons and holes), 2) phonon emission and 3) photon emission.

5 The discovery of these pre-equilibrium emissions provides new pathways to convert the high grade chemical energy available during pre-equilibrium phases into useful work. The term "pre-equilibrium" refers to the period, however brief, during which the products of reactions have not yet come to
10 thermal equilibrium. These products include energy emissions, such as charge carriers; high frequency phonons normally associated with the optical branch lattice vibrations and with acoustic branch vibrations of similar wavelength and energy; and excited state chemical product species.

15 Prior to the discovery of these rapid energy emission pathways, the energies resulting from a catalytic process, such as the heat of adsorption and the heat of formation, were considered to be heat associated with an equilibrium
20 condition. Indeed, after tens of femtoseconds, emitted charge carriers have thermalized and after a few to hundreds of picoseconds, emitted phonons have thermalized.

Summary Of The Invention

In an exemplary embodiment of the present invention, the
25 emissions of charge carriers, such as electron-hole pairs,

generated by chemical activity and reactions on or within catalyst surfaces, clusters or nanoclusters, are converted into electric potential. In an exemplary embodiment, semiconductor diodes such as p-n junctions and Schottky diodes
5 formed between the catalyst and the semiconductors are used to carry out the conversion. The diodes are designed to collect ballistic charge carriers and can be Schottky diodes, pn junction diodes or diodes formed by various combinations of metal-semiconductor-oxide structures. The interlayer oxide
10 thickness is preferably less than the particular ballistic mean free path associated with the energy loss of the appropriate charge carrier (e.g., hole or electron). The diodes are placed in contact with or near the catalyst nanolayer or nanocluster within a distance whose order of
15 magnitude is less than approximately the mean free path of the appropriate ballistic charge carrier originating in the catalyst. In one embodiment, the diode is located adjacent to the catalyst cluster, while in a further embodiment, the diode is located under the catalyst, as a substrate.

20 The charge carriers travel ballistically over distances that can exceed the width of appropriately fabricated semiconductor junctions, similar to a thermionic effect. However, unlike the thermionic effect, the charge carriers in the case of the present invention need not have energy greater
25 than the work function of the material involved. The charge

carrier motion is trapped as a difference in fermi level, or chemical potential, between either side of the junction. The resulting voltage difference is indistinguishable from that of a photovoltaic collector. However, the charge carrier forces
5 itself into the valence or conduction band and the circuit provides a counterpart hole or electron.

The present invention also provides devices and methods for converting the energy generated by catalytic reactions to mechanical motion before the energy thermalizes. In an
10 exemplary embodiment, the converted motion is used to move a hydraulic fluid against a resisting pressure.

Recent advances in the art of quantum wells, atomically smooth superlattices and nanometer scale fabrication permit a degree of tailoring of the physical parameters to favor a
15 particular reaction pathway (charge carrier, phonon, photon) or to enhance the efficiency of the energy collector.

The temperature of operation of a device in accordance with the present invention can be as low as hundreds of degrees Kelvin, which is much lower than the typical
20 operational temperatures of conventional thermophotovoltaics and thermionic systems (1500 to 2500 Kelvin). Moreover, the power per mass and power per volume ultimately achievable using pre-equilibrium emissions in accordance with the present invention exceeds that of fuel cells, conventional thermo-
25 photovoltaics, and conventional thermionic systems.

Furthermore, in comparison to fuel cells which require complex ducting, the devices of the present invention allow mixing of fuel and air in the same duct, thereby simplifying ducting requirements.

5 The combination of high volume and mass power density, simplicity, and lower temperature operation makes the methods and devices of the present invention competitive and uniquely useful.

10 Brief Description Of The Drawing

FIG 1. shows a cross-section of an exemplary embodiment of a device for generating electricity in accordance with the present invention.

15 FIG. 2 shows a cross-section of an exemplary embodiment of a device for converting the energy released by a catalytic reaction into mechanical work.

FIG. 3 shows a cross-section of an exemplary embodiment of a device for generating electricity piezoelectrically.

20 FIG. 4 shows an exemplary embodiment of an arrangement for generating electricity or radiation beams in accordance with the present invention.

Detailed Description

FIG. 1 shows a cross-sectional view of an exemplary embodiment of a device in accordance with the present invention. The device of FIG. 1, includes a catalyst 105 which is arranged on a top surface of the device to come into contact with oxidizer molecules 103 and fuel molecules 102. In the exemplary embodiment of FIG. 1, the catalyst 105 can be comprised of platinum or palladium, the oxidizer 103 can be comprised of air and the fuel 102 can be comprised of hydrogen or a reactant hydrocarbon such as methanol or ethanol.

Exhaust molecules 104 result from the catalyzed reaction.

The exemplary device of FIG. 1 comprises a pair of Schottky diodes which act as charge carrier collectors, with one diode 113 being arranged on the top surface of the device, adjacent to the catalyst 105 (the "adjacent surface diode") and the other diode 109 being arranged in the substrate 108, below the catalyst (the "substrate diode"). An insulating layer 111 is arranged between the adjacent surface diode 113 and the substrate 108, as shown. The diodes 109 and 113 preferably comprise a bipolar semiconductor material such as InGaAsSb with a composition chosen to optimize the chosen operating conditions. For example, the second harmonic of a CO stretch vibration on a catalyst surface at 2340 per cm energies gives a photon energy of 0.58 eV. (This matches the 0.53 eV band gap of a recently developed InGaAsSb diode described in G.W. Charache et al., "InGaAsSb

thermophotovoltaic diode: Physics evaluation," Journal of Applied Physics, Vol. 85, No. 4, Feb. 1999). The diodes 109 and 113 preferably have relatively low barrier heights, such as 0.05 to 0.4 volts.

- 5 The substrate diode 109 should be forward biased sufficiently (e.g., up to 3 volts) to raise its conduction and valence bands above the fermi level of the catalyst 105 so as to match the energy levels of the adsorbed reactants on the catalyst surface, such as oxygen or hydrocarbon free radicals.
- 10 This induces resonant tunneling of energy into the substrate diode 109 by photons. The dimension of the oxide barrier or the depletion region should be kept to less than the ballistic transport dimension, which is on the order of 10 nanometers.

- A metal such as Mg, Sb, Al, Ag, Sn Cu or Ni may be used
- 15 to form an interlayer 106 between the catalyst 105 and the semiconductor of the substrate diode 109. The interlayer 106 serves to provide a lattice parameter match between the catalyst material and the substrate, which in turn provides a smooth and planar interface surface with which to construct a
- 20 quantum well structure consisting of the catalyst, the vacuum above and the interlayer below. A quantum well structure with smooth interfaces alters the density of electron states in the directions toward the substrate and toward the vacuum, so as to enhance the number of electrons with the desired energy.
- 25 The thickness of the catalyst and the interlayer should be

small enough to permit ballistic transport of charge carriers. This dimension is typically less than 20 nanometers. Quantum well structures with thickness less than 0.5 nanometer are possible in the present state of the art. The quantum well
5 structure may be constructed as an island, like a pancake on a surface (also referred to as a "quantum dot").

The device of FIG. 1 may also include a non-conducting layer 107 arranged between the substrate diode 109 and the catalyst 105. The layer 107, which can be comprised of an
10 oxide, permits forward-biasing of the diode 109 without a significant increase in the forward current. The layer 107 provides a barrier against such forward current. An optional oxide 114 barrier may also be arranged on the surface of the device between the catalyst 105 and the surface diode 113.

15 Electrical contacts 101, 110 and 112 are arranged as shown in FIG. 1. Contacts 101 and 110 serve as electrical output leads for the substrate diode. Contacts 101 and 112 are the electrical output leads for the surface diode.

In the device of FIG. 1, the catalyst layer 105 may
20 comprise a quantum well structure (including quantum dots) having a thickness typically less than 20 nm and being sufficiently small so as to alter the density of electron states in the catalyst to favor the production of substantially monoenergetic holes or electrons. The substrate
25 diode 109 and the catalyst 105 may be separated by an

interlayer 106 of metal that permits matching the lattice parameters of the catalyst to this interlayer. The catalyst 105 and interlayer 106 comprise the quantum well. The interlayer 106 must be sufficiently thin so as to permit non-
5 energy changing electron transport into the diode. The thickness of the interlayer 106 should be preferably less than 20 nanometers.

In an exemplary embodiment of a device in accordance with the present invention, the substrate diode 109 comprises an n-
10 type direct band gap semiconductor with a band gap chosen to favor the emission of energetic electrons.

In a further exemplary embodiment, the thickness or cluster size (if arranged in clusters) of the catalyst layer 105 is sufficiently small so as to permit the appearance of
15 band gaps, discrete electron states and catalyst properties unlike the same material in bulk. In this case, the catalyst 105 can be comprised, preferably, of gold, silver, copper, or nickel and be arranged as monolayer, 200 atom clusters.

FIG. 2 shows an exemplary embodiment of a device in
20 accordance with the present invention in which the emissions of phonons generated by adsorbing and bonding reactions on or within catalyst surfaces, clusters or nano-structures are converted into hydraulic fluid pressure.

In accordance with the present invention, pressures
25 generated by phonons directed into a catalyst body on a first

side of the catalyst body form a phonon wave which can be guided by the geometry of the catalyst (or substrate upon which the catalyst may be situated) so that the phonons travel to the other side of the substrate and impart a pressure onto
5 a fluid. The thickness of this travel should be less than the mean distance over which the direction of the phonon remains substantially unperturbed. The phonons arrive at an angle (a "grazing" angle) such that the directional and asymmetric pressure of the arriving phonons appears as wave motion on the
10 other side of the catalyst body which pushes against a fluid such as a liquid metal or sacrificial interface, causing it to move in a direction parallel to the bottom surface. An apparent negative coefficient of friction between the wall and the fluid is exhibited due to the wave motion or directed
15 impulses along the surface of the bottom of the device.

The exemplary device comprises a substrate 202 with top and bottom surfaces having a saw-tooth pattern, as shown in the cross-sectional view of FIG. 2. The bottom surface is in contact with a hydraulic fluid 204. As shown in FIG. 2, the
20 substrate can be thought of as comprising a plurality of sub-structures 200 having rectangular cross-sections and arranged adjacent to each other at an angle with respect to the hydraulic fluid 204.

At the top surface of the substrate, each sub-structure
25 200 includes a layer 201 comprising a catalyst. On an exposed

side surface between adjacent sub-structures, each sub-structure 200 includes a layer 202 of material which is inert with respect to the catalyst and the reactants. The body of each sub-structure is comprised of a substrate 203, which also
5 acts as a phonon waveguide. Platinum can be used for the catalyst layer 201 and for the substrate 203 with air as the oxidizer, ethanol or methanol as the hydrocarbon reactant fuel and water or mercury as the hydraulic fluid 204. The hydraulic fluid can also serve as a coolant for the device,
10 thereby permitting high power density operation.

The catalyst 201 and substrate 203 may be comprised of the same material, e.g., platinum. Other substrate materials may be used based on structural considerations, manufacturability and/or impedance matching so as to maximize
15 the propagation of the phonon motion into the hydraulic fluid.

The thickness of the platinum catalyst layer 201 and substrate 203 should be less than the energy-changing mean free path of optical branch phonons or high frequency acoustic branch phonons, which is at least of order 10 nanometers and
20 can be as large as one micron.

Nanofabrication methods can be used to form the sawtooth patterns on the surfaces of the substrate 202, with the dimension of a unit of such pattern being as large as 1 micron.

By depositing the inert layers 202 as shown, e.g., on the right-facing facets of the saw-tooth pattern of the top surface, a preferential direction is thereby established for reactions and thus for phonon propagation, as indicated by the
5 arrow in FIG. 2.

Acoustic, ultrasonic or gigahertz acoustic Rayleigh waves on the catalyst side can be used to stimulate the reaction rate and synchronize the emission of phonons. The waves increase the magnitude of the phonon emission and cause
10 coherent emission, greatly enhancing both the peak and average power.

In a further embodiment, a thin layer or layers of material are arranged between the substrate and the fluid. These layers are comprised of materials having acoustic
15 impedances between that of the substrate 202 and the hydraulic fluid 204, so as to maximize the transmission of momentum into the hydraulic fluid and minimize reflections back into the substrate 204. The material should be selected so that the bulk modulus and phonon propagation properties of the material
20 cause the phonons emerging from the substrate to be transmitted substantially into the fluid with minimal reflection and energy loss.

In a further embodiment of a device in accordance with the present invention, the emissions of phonons generated by
25 catalytic reactions are converted into electrical current by

piezo-electric effects within materials as the phonons impact the materials. An exemplary embodiment of such a device is shown in FIG. 3.

The exemplary device of FIG. 3 comprises a catalyst layer 301 arranged on a piezo-electric element 303, which is in turn arranged on a supporting substrate 304. The catalyst layer 301 can be implemented as a nanocluster, nanolayer or quantum well. Electrical leads 302 are provided at opposite ends of the piezo-electric element 303 across which a potential is developed, in accordance with the present invention. In the exemplary embodiment of FIG. 3, the catalyst layer 301 comprises platinum, with air as the oxidizer and ethanol or methanol as the hydrocarbon reactant fuel. The piezo-electric element 303 can comprise any piezomaterial, including semiconductors that are not normally piezoelectric, such as InGaAsSb. The lattice mismatch between the semiconductor and the platinum produces a strain, commonly called a deformation potential which induces piezoelectric properties in semiconductors, or ferroelectric or piezoelectric materials with a high nonlinearity such as (Ba, Sr)TiO₃ thin films, Al_xGa_{1-x}As/GaAs and strained layer InGaAs/GaAs (111)B quantum well p-i-n structures.

Where the piezoelectric element 303 is comprised of a semiconductor, the semiconductor becomes a diode element that

converts photons into electricity, collects electrons as electricity, and converts phonons into electricity.

In the exemplary embodiment of FIG. 3, as the reactants interact with the catalytic layer 301, phonons generated by the reactions are conducted into the piezoelectric material 303. As a result, a potential is induced in the piezoelectric material 303 at the electrical contacts 302.

The geometry of the substrate 303 is preferably such as to focus phonons so as to enhance the nonlinearity of the piezoelectric element 303. This results in self-rectification of the high frequency phonons. In an exemplary embodiment, the piezoelectric element 303 is preferably curved and shaped like a lens or concentrating reflector so as to focus the phonons generated by the catalyst on to the piezoelectric material. The focusing of the phonons causes large amplitude atomic motions at the focus. The atomic motions induced by this focusing cause the piezoelectric material to become nonlinear, causing non-linear responses such as the generation of electricity in the material at the focus. This in turn results in the piezo-material becoming a rectifier of the phonon-induced high frequency current.

Acoustic, ultrasonic or gigahertz acoustic Rayleigh waves can be used on the catalyst side of the exemplary device of FIG. 3 to stimulate the reaction rate and synchronize the emission of phonons, to enhance the magnitude of the phonon

emission and to cause coherent emission, greatly enhancing both the peak and average power delivered to the piezoelectric material 303. Acoustic Rayleigh waves accelerate oxidation reactions on platinum catalyst surfaces. Surface acoustic waves can be generated on the surface of the catalyst 301 using a generator (not shown). Such waves may have acoustic, ultrasonic or gigahertz frequencies. The Rayleigh waves induce reactions so as to synchronize the reactions, which in turn synchronizes the emission of phonons. The result is a pulsing bunching of the reactions, which enhances the power delivered to the piezoelectric material 303.

The frequency of operation of the device of FIG. 3 is preferably in the GHz range and lower so that rectification of the alternating currents produced by the piezoelectric material 303 can be achieved with conventional means, such as with semiconductor diodes.

In a further exemplary embodiment of the present invention, electromagnetic radiation, such as infrared photons emitted by excited state products such as highly vibrationally excited radicals and final product molecules, is converted into electricity photovoltaically. Stimulated emission of radiation is used to extract the energy from the excited state products, such as highly vibrationally excited radical and reaction product molecules both on the catalyst surface and desorbing from it. The extracted energy appears in the form

of a coherent beam or a super-radiant beam of infra-red or optical energy. The frequencies of the radiation correspond to fundamental (vibration quantum number change of 1) or overtones (vibration quantum number change 2 or greater) of the normal mode vibration frequencies of the reactants.

Several different frequencies may be extracted simultaneously in this invention. While the resulting coherent beam is useful in its own right, this high intensity beam can also be photovoltaically converted into electricity. In accordance with the present invention, such emissions are created by reactions on catalyst surfaces, and are accelerated by the use of optical cavities. FIG. 4 shows an exemplary embodiment of an electric generator for performing such a conversion.

The device of FIG. 4 comprises one or more substrates 401 upon which a catalyst 402 is arranged in a plurality of islands, nanoclusters, quantum well clusters or quantum dots. The catalyst clusters are sufficiently spaced apart (e.g., tens of nanometers or more) and the substrate is made sufficiently thin (e.g., less than a centimeter total optical thickness), so that IR absorbtion is mitigated at the frequencies of specie emission. The assembly of catalyst clusters on the substrates 401 is substantially transparent to the reaction radiations. The catalyst 402 is preferably platinum or palladium. The device preferably comprises a

plurality of substrates 401 stacked so as to permit a volume of reactions.

The catalyst-substrate stack 401/402 is enclosed in an optical cavity having a highly reflective element 403 and a less reflective element 404 arranged as shown in FIG. 4. The optical cavity and the catalyst-substrate stack 401/402 are preferably resonant to the reaction radiations or their overtones. The optical cavity can be used to stimulate overtone radiation, i.e., multipole radiation where the change in quantum number is 2 or more, to increase the energy of the radiation. The optical cavity preferably has multiple frequencies, as in a Fabrey-Perot cavity, that are tuned to overtones of the specie frequencies.

A fuel 407, such as hydrogen, ethanol or methanol and an oxidizer 408, such as air, are introduced into the optical cavity where they interact with the catalyst-substrate stack 401/402. Lean mixtures of fuel can be used so as to minimize resonant transfer, exchange or decay of excited state vibrational energy to other specie of the same chemical makeup in the exhaust stream, during the time these species are in the optical cavity and the photovoltaic converter 405 collects the radiation and converts it into electricity.

A stimulated emission initiator and synchronizer device 412 is used to initiate and synchronize the emissions in the optical cavity. The device 412 can be a commonly available

stimulated emission oscillator and can be coupled to the device of the present invention in known ways. The optical cavity can be designed in a known way to create stimulated emission of radiation. A photovoltaic cell is typically not
5 very efficient in converting long wavelength IR photons (1000 to 5000 per centimeter) characteristic of the catalytic reactions. The high peak power output of the device 412 remedies this situation and makes the IR photovoltaic cell more efficient.

10 A photovoltaic converter 405 is placed outside the volume of the catalyst-substrate stack 401/402 anywhere visible to